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A basin scale perspective on CO_2 storage – short and long term risks

Harald Johansen[a]*

[a]*Institute for Energy Technology, P.O.Box 40, NO-2027, Kjeller, NORWAY*

Abstract

The CO_2 retention capacity of sediments is a very important control on the long term CO_2 content of the atmosphere. When CO_2 is stored at depths exceeding c. 800-1000 m, several important overburden sinks prevent CO_2 from returning to the atmosphere. In addition to seal capacity, CO_2 is immobilized by dissolution in overburden formation water, by sorption onto mineral surfaces and organic matter, by anionization during carbonate dissolution, and by mineralization. The purpose of this presentation is to show that the combined capacity of sinks in overlying sediments is most likely much in excess of the need for permanent storage, and that mineral reaction rates are fast enough to benefit from the sinks. There is however a need to improve the data background which is supporting this tentative conclusion. Basin scale natural CO_2 processes and the baselines associated with them, have so far been only weakly constrained. In particular better quantitative constraints are needed on the magnitude of natural CO_2 sources, reservoirs and sinks, before realistic retention capacities of overburden sediments may be estimated.
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1. Introduction

Carbonate minerals are the dominating reservoirs for CO_2 in sedimentary basins, but also organic matter is an important reservoir/source. Precipitation and dissolution of carbonates depends on pressure, temperature, depth, salinity, pore water and sediment composition. Thermal and biogenic gas generation has the potential to exsolve gas from water and oil, and thereby contribute strongly to gas migration. Various natural gas components (CO_2 , CH_4, H_2S and H_2) have strongly contrasting properties with respect to reactivity, solubility in water, sorbability, capillary resistance and density. Also injection gas impurities (SO_x, NO_x, N_2, O_2, amines) may be present, and modify gas mixture behavior. Sorption/desorption and solution/exsolution of various gas components depend, in addition to pressure, depth, temperature and salinity, on their mutual interactions. Any attempt to model or predict accumulation

* Corresponding author. Tel.: +47-6380-6148; fax: +47-6381-5553.
E-mail address: hjo@ife.no.

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or leakage of various gas components, must in addition to considering sedimentary baselines, also control interactions in multicomponent, multiphase systems.

The first row of "defense" in the overburden above a CO_2 storage will be sorption and aqueous solution. Kinetically speaking these processes are fast, and their capacity can be utilized on the timescale of injection. CO_2 in overburden sediments may however contribute to CH_4 liberation, because this component has a lower solubility in water, and also lower sorbability than CO_2. Carbonate and silicate dissolution are much slower processes (second and third lines of defense). To what extent the full capacity of mineral dissolution will contribute to immobilization of CO_2 in the overburden, is a central topic of this paper. CO_2 storage capacity is usually calculated as the amount that can be stored in a porous sediment beneath an effective seal. While this is relevant for the injection time scale, long term storage capacity should also include overburden sediments. Given that the tentative conclusions in this paper turn out to be valid, the main concern should therefore ultimately be towards the injection time scale, and towards shortcut migration paths, like faults, fractures and wells.

2. Method and data background

In order to quantify the long term retention capacity of the overburden, data from earlier diagenetic studies of a large number of wells from the Norwegian Continental Shelf, including sandstone, mudrock and limestone lithologies, has provided an adequate database for lithology, mineralogy, and sediment reactivity. Composition and isotopes from minerals, waters and gases, experimental data on natural CO_2 generation from organic sources, and an empirical model for natural CO_2 source strength [1], has been additional data sources and tools. Important CO_2 reservoirs, sinks and sources, aqueous solubility and migration fluxes have been quantified for a wide range of lithologies typical for overburden sediments.

Table 1 Mudrock Database

Sample types	Activity
Lithologies	Mudrocks, shales, marls, limstones, sandstones
Mineralogy	XRD, SEM
Petrography	SEM, optical microscopy
Organic analysis	RockEval, Elemental composition, Hydrous Pyrolysis
Composition	Water, gas, pyrolysis products
Isotopes	Water, gas, pyrolysis products

Literature kinetic data have been used to quantify rates of important dissolution and precipitation reactions. Constraints on CO_2 sorption are from [2]; on aqueous solubility of CO_2 from [3]; and on mineral thermodynamics and kinetics from [4].

3. Results and discussion

The discussion of CO_2 retention capacity of overburden sediments focuses on the following topics:

1) Processes and baselines for CO_2 in overburden sediments
2) Natural CO_2 sources
3) CO_2 reservoirs
4) Natural CO_2 sinks
5) Retention capacity of CO_2 in the overburden

3.1. Processes and baseline for CO_2

Data from mudgases collected during exploration drilling, and gases from various well ringrooms from producing wells, has revealed a generalised depth pattern for natural gas occurrence. In this scheme 5 successive depth zones are identified (from seabottom downwards):

1) Bacterial sulphate reduction zone (less than 100 m)
2) Methane rich zone (CO_2 reduction zone; down to a few hundred meters)
3) Gas poor zone (biogenic gas; down to nearest reservoir)
4) Hydrocarbon reservoir (with/without biogenic gas)
5) Source rock (zone of thermal gas generation (3-10 km)

In terms of CO_2 supply or consume, the zone characteristics are:

1) HCO_3^- (CO_2) formation
2) CO_2 consumption
3) Bacterial CO_2 generation
4) Bacterial and/or thermal CO_2 generation
5) Thermal CO_2 generation

Extensive and repetitive sampling of gases from mid ringrooms of wells from the giant Troll gas field in the North Sea (Troll A platform; shoe level 750 m below sea bottom) has revealed very low absolute gas contents, as well as very high H_2/CH_4 ratios, low CO_2 contents, and clear signatures of biodegradation of propane (C isotopes). The outer ringroom gases (shoes at 120 m below seabed) contrasts strongly with mid ringroom gases: having a high gas content; dry methane gas; isotopically light biogenic signatures. Shirt cells a few tens of meters below the seabed are gas lean and heavier isotopically. Formation water data show that bacterial sulphate reduction is responsible for the low gas content and heavy C isotopes of CH_4 from this zone. Mudgas and test gas data from exploration wells confirm the same overall depth zonation. In the Troll area a distinct CH_4 $\delta^{13}C$ gradient is seen from the reservoir to 300 m below seabed, with a reversal to more heavy C isotope values at shallower depth. Similar reversals are seen in most North Sea shallow sediments. Reversal depth varies between 300 and 900 m below the seabed. This corresponds fairly well with the top of the interval where CO_2 solubility reverses from increasing solubility shallower than about 500 m, to decreasing solubility with increased depth below 500 m. A

Table 2 Properties of some natural gas components

Gas properties	H2	CO2	CH4	H2S
reactivity	**high**	**high**	**low**	**high**
solubility in water	**very low**	**high**	**low**	**high**
sorbability	**low**	**high**	**mod**	?
capillary resistance	**low**	**mod**	**mod**	**mod**
density	**low**	**high**	**mod**	**high**

precise explanation for these patterns is difficult to give, but in a general way biodegradation of oil and gas to CO_2 and organic acids, with subsequent CH_4 formation from these substrates, must be involved. As CO_2 seems to be an important intermediate product of biodegradation, the CO_2 baseline will be strongly affected by hydrocarbon migration patterns. The gas products of biodegradation (H_2, CH_4, CO_2, H_2S) do however show large differences with respect to volatility and aqueous solubility.

3.2. *CO_2 sources in sedimentary basins*

3 fundamentally different processes can generate CO_2 in sediments: 1) Bacterial activity, 2) Thermal maturation, and 3) carbonate dissolution.

In the next section the magnitude of the diagenetic carbonate pool will be discussed. Figure 1 shows C isotope signatures of carbonate cements from North Sea sandstones and mudrocks. The dominating occurrence of strongly negative and positive isotope values show that the organic CO_2 input to carbonates is huge, supporting the idea discussed above that biodegradation is a very important source of CO_2. Along normal geothermal gradients (say 35°C/km) at hydrostatic pressure, calcite has a maximum in solubility in the depth interval 250-500 m blow seabed [5]. Below this zone, down to 2 km, a 50% decrease in solubility is seen. Ascending gas will therefore also tend to lose CO_2 to carbonate precipitation up to 250 m below the seabed. The isotope homogenization at large depth is therefore not driven by temperature increase, but is suggested to be driven by dissolution caused by organic CO_2 input. The thermal generation of CO_2 (and hydrocarbon gases) was studied by Barth et al [1]. The genetic potential of CO_2 as quantified from hydrous pyrolysis of mudrocks, show that a high CO_2 potential persists to great depths: 40-50 % of the CO_2 generating potential is still present at 5 km depth. We also observe that mineral composition exerts some control on the potential, most likely through the pH control on CO_2 solubility in water and the sorption equilibria with mineral surfaces. Carbonate rich sediments (alkaline formation water) have a higher CO_2 generation potential than kaolinite rich sediments (acidic formation water). It is believed that CO_2 sorption is part of the explanation of the high remaining CO_2 generation potential at great depths.

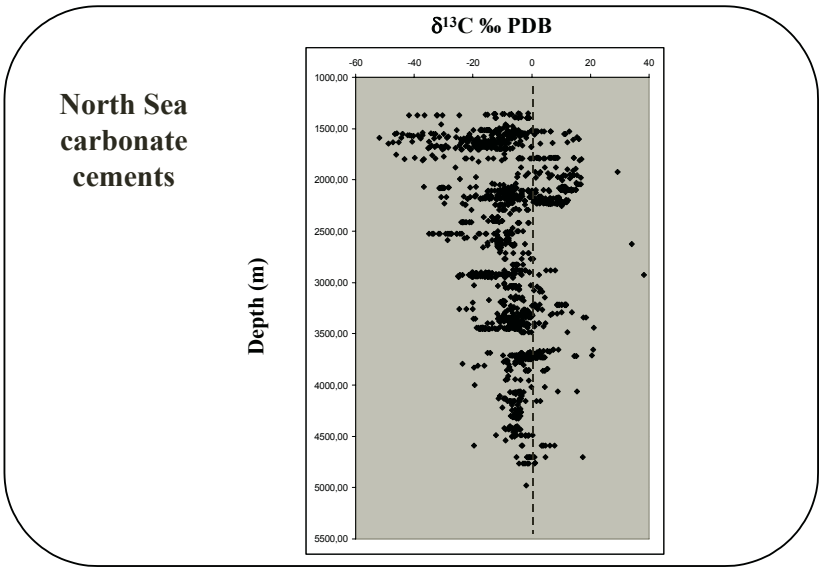


Figure 1. C isotope values of North Sea carbonate cements in mudrocks and sandstones.

CO_2 reservoirs in sedimentary basins

Solubility of CO_2 in formation water depends mainly on pressure, temperature and salinity. Using 0.6 m NaCl as a mean value for mudrock pore water (same salinity as sea water), 20% sediment porosity, and the solubility model of Duan et al, 2003, each m3 of sediment may contain up to 26.4 kg CO_2 dissolved in water. We lack data for pore water outside reservoirs, but it is likely that such waters are generally far from being CO_2 saturated. CO_2 dissolution in water is therefore a powerful sink for CO_2. If the formation water had been saturated, c.1/3 of all the CO_2 in the sediments would have been contained in aqueous solution (see calculations below).

Figure 2 shows how CO_2 and CH_4 solubility varies with temperature for a thermal gradient of 35°C/km, at 0.6 m NaCl and 3 m NaCl salinity, respectively. For the first 0.5 km of burial, CO_2 will be increasingly soluble in water, then for the next 1.5 km down to 2 km solubility is reversed. CH_4 solubility shows a much more smooth increase, but the value is much lower than for CO_2. Gas that is migrating upwards in a sedimentary basin along a geotherm of 35°C/km at hydrostatic pressure will show CO_2/CH_4 fractionation due to different solubility-depth trends for the two gases. The contrast is particularly clear between 35-60°C (1-2 km), where the CO_2/CH_4 ratio in the gas will tend to decrease upon gas ascent.

Carbonate cement and limestone is the dominating reservoir of CO_2 in sediments. In our North Sea database, excluding the amount of carbonate in Cretaceous chalks and marls (which is huge), carbonate cements represent more than 50% of the CO_2 in the sediments. The arithmetic mean value for carbonate content in North Sea mudrocks is 12.9 % based on XRD data. This corresponds to 44 kg CO_2 per m^3 sediment at 20% porosity.

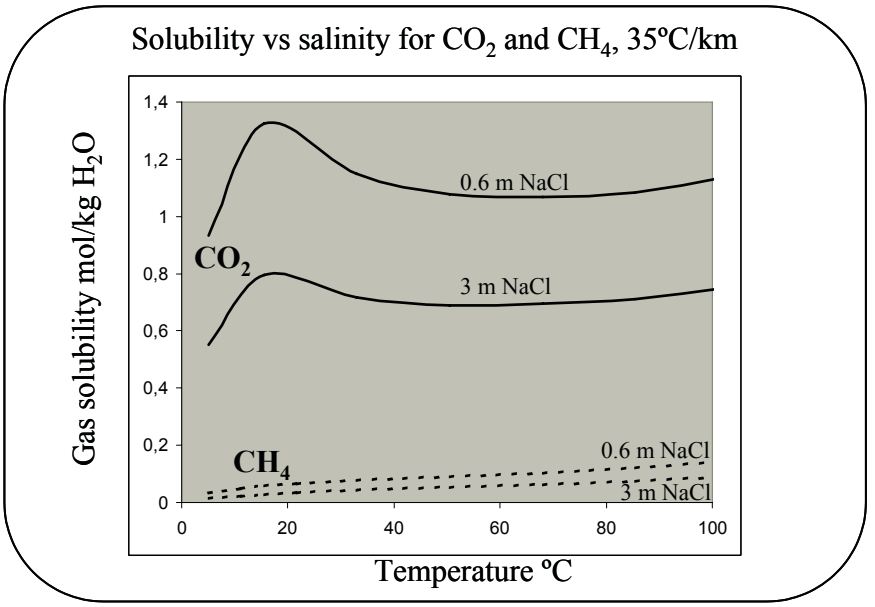


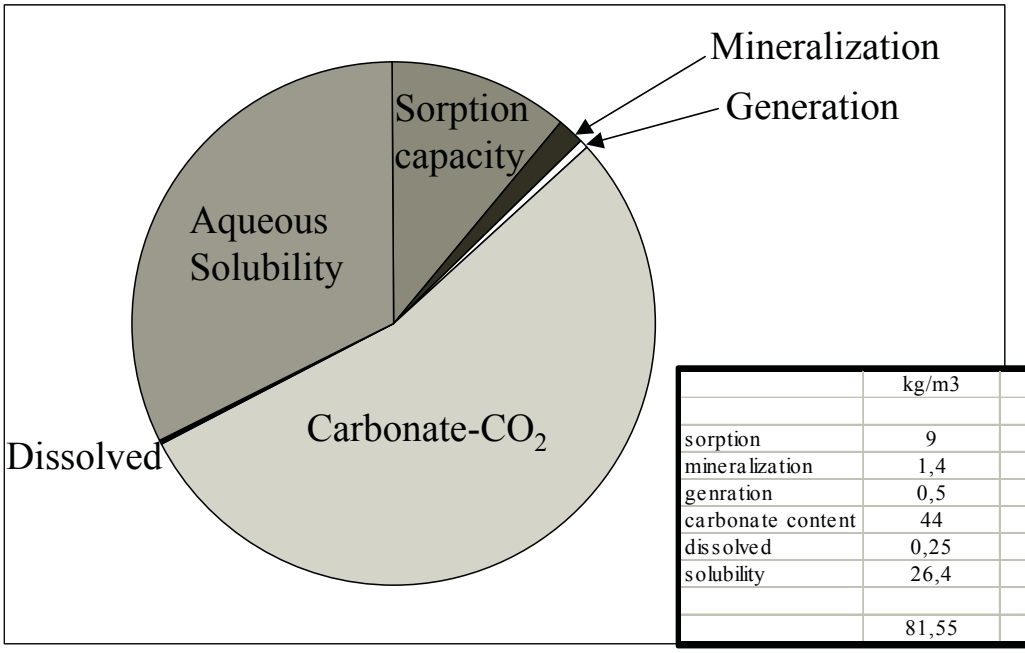
Figure 2. Solubility of CO_2 and CH_4 in saline waters

We have much less data support for estimates on how much CO_2 that is adsorbed in the sediments, and for the maximum sorption capacity. Some experimental data is given in Busch et al [2]. On this basis we may calculate a maximum sorption capacity of 9 kg pr m^3 sediment (20% porosity).

3.3. CO_2 sinks in sedimentary basins

The amount of non-carbonates in mudrocks that may be reacted by CO_2 to form carbonates depends on the content of divalent metals. Using plagioclase as an example, 2vol% of this mineral with a Ca/Na ratio of 0.18 may form 1.4 kg calcite per m3 of sediment, which is only 3% of that already present as carbonate. $\delta^{13}C$ values of carbonate cement (figure 1) demonstrate that a very large proportion of the carbonatization potential has already been utilized. Distribution of light and heavy values, and the depth trend, together indicate that a very high proportion of the C in carbonates is of organic origin, and that the interval down to 2.5 km is responsible for a large proportion of the organic sourcing. Below 2.5 km the depth trend converges towards intermediate isotope values, which is most likely a result of extensive carbonate recrystallization, and sorption and desorption of CO_2.

Anaerobic bacterial reduction of CO_2 to CH_4 is another mechanism that works as a CO_2 sink, but the other side of the coin is that an equivalent amount of CH_4 is replacing CO_2. CH_4 is less water soluble, and less sorbable than CO_2, so this process may alternatively be a greenhouse gas source, depending on the possibility to trap or produce the methane. Carbonate cement data from the Frigg Field in the North Sea is a particularly interesting example. The strongly ^{13}C enriched carbonates from this field demonstrates that CO_2 reduction may be a quantitatively very important process.



	kg/m3	%
sorption	9	11,0 %
mineralization	1,4	1,7 %
genration	0,5	0,6 %
carbonate content	44	54,0 %
dissolved	0,25	0,3 %
solubility	26,4	32,4 %
	81,55	100,0 %

Figure 3. Important CO_2 sources and reservoirs in sediments

Figure 3 illustrates the relative capacities and reservoir sizes for solubility, sorption, mineralization and generation, compared with the carbonate content. The very small amount of CO_2 assumed to be dissolved in mudrock formation waters, suggests that solid carbonates and biogenic CH_4 are the most stable final products of the sedimentary C processes.

3.4. CO_2 retention capacity of sedimentary basins

Around 12 million tons of CO_2 has so far been stored in Utsira sands above the Sleipner field. If we consider a 900 m thick prism of overburden sediments with the same surface area as the CO_2 accumulation in Utsira, an additional 50 million ton capacity for storage and immobilization is represented by aqueous solubility, sorption, anionization by carbonate dissolution, and carbonatization of non-carbonate minerals in the overburden. This buffer storage capacity is even larger when we consider lateral expansion of the leakage plume in overburden sediments, which is very likely.

The "first row of defense" in the overburden is sorption and aqueous solution of CO_2, which occurs almost instantaneously. The total capacity of this barrier can be estimated to 32 Mt of CO_2, minus baseline values. A "flaw" in this defense is that some baseline CH4 will become desorbed and exsolved.

The "second row of defense" in the overburden is dissolution and subsequent anionization of pre-existing carbonates. Assuming a characteristic rate constant for the dissolution process to be 1e-6 mol/m^2·s, a total overburden immobilization capacity of 400 Mt CO_2/y is calculated. From the mudrock carbonate pool of 44 kg/m^3, an anion storage capacity for the whole overburden of 17.4 Mt CO_2 is calculated, which indicates that carbonate dissolution is fast enough to be a short-term barrier.

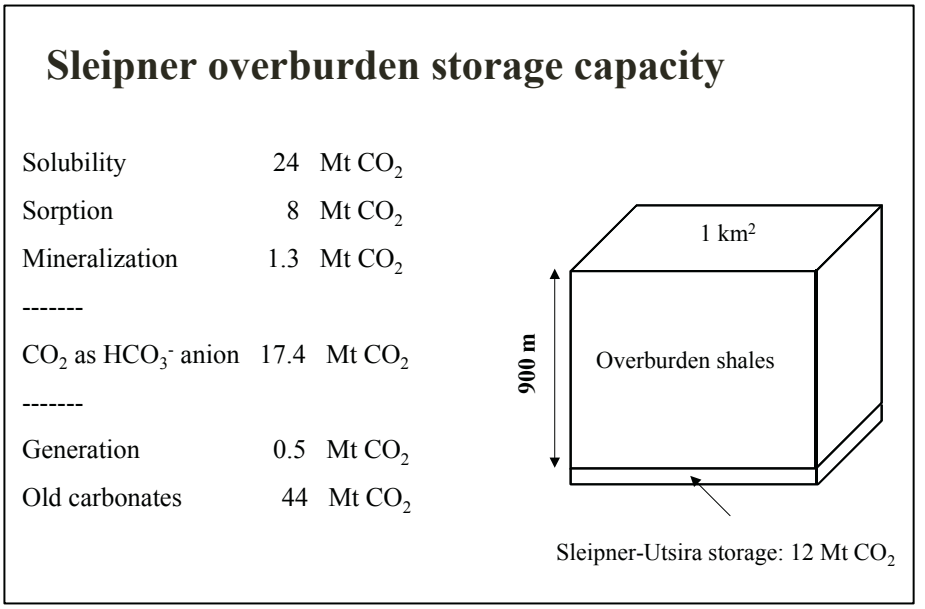


Figure 4. CO_2 budget for overburden sediments

The "third row of defense" is the dissolution of non-carbonate minerals (mainly silicates) and the associated carbonatization of released divalent cations. If we assume that 2 vol% plagioclase with 15% Anorthite component is still present in the overburden sediments, and that the characteristic rate of silicate dissolution in the vicinity of a CO_2 plume is around 1e-9 mol/m^2·s (in-house experimental data), a carbonatization capacity of c. 0.4 Mt CO_2/y is estimated. In a perspective beyond the injection time scale, even the slowest mineral reactions will proceed fast enough to take advantage of the full carbonatization capacity of the overburden. Although precise calculation of overburden retention capacity is impossible, it is clear from this work that this capacity may by far exceed the storage capacity of primary storages.

4. Conclusions

Overburden thickness, porosity and chemical (mineralogical) composition should be included in regulations to give credit for stored CO_2. A global subsurface CO_2 storage capacity of c. 2000 Gt in primary storages has been estimated. We should add an additional much larger overburden retention capacity (albeit difficult to quantify accurately with the present data background). Compared with this, an annual CO_2 storage need of 15-20 Gt/y seems quite moderate. Even a total amount of c. 750 Gt CO_2 in the atmosphere is much less than the total subsurface storage capacity. If the tentative estimates of overburden storage capacity of this study turn out to be valid, a consequent suggestion will be to put increased focus on shortcut migration paths and on injection time scale, rather than long term storage and retention capacity. Monitoring efforts should then also be focussed towards shortcut (short term) pathways. When short time leakage paths can be ruled out, adequate remediation plans exist, and overburden is thick enough, storage credits should be given.

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